

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
24 March 2005 (24.03.2005)

PCT

(10) International Publication Number
WO 2005/026086 A1

- (51) International Patent Classification⁷: **C07C 5/02**, (74) Agent: WESTBY, Timothy, S.; CONLEY ROSE, P.C.,
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- (21) International Application Number: PCT/US2003/038871 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 5 December 2003 (05.12.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/499,841 3 September 2003 (03.09.2003) US
60/499,839 3 September 2003 (03.09.2003) US
10/728,310 4 December 2003 (04.12.2003) US
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- (84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR LIQUID PHASE HYDROGENATION

(57) Abstract: A process for the liquid phase selective hydrogenation of alkynes to alkenes with high selectivity to alkenes relative to alkanes, high alkyne conversion, and sustained catalytic activity comprising a reactant comprising an alkyne and a non-hydrocarbon solvent/absorbent, contacting the reactant stream with a hydrogen-containing stream in the presence of a supported, promoted, Group VIII catalyst, removing the solvent/absorbent, and recovering the alkene product.



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PROCESS FOR LIQUID PHASE HYDROGENATION

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates generally to the selective hydrogenation of unsaturated compounds to more-saturated analogs. In particular, alkynes are converted to alkenes by hydrogenation of the alkynes over a fixed bed of supported catalyst, while in an absorptive non-hydrocarbon absorbent.

Description of the Related Art

Hydrogenation of alkynes and/or multifunctional alkenes to compounds containing only one alkene group is an important industrial process and is discussed widely in the patent literature. Acetylene, the simplest alkyne, occurs in many processes as a main product or by-product which is thereafter converted to ethylene or ethane by hydrogenation. Thermal cracking of ethane can be caused to produce mostly ethylene, but a minor undesired product is acetylene. Pyrolysis of simple alkanes or mixtures containing primarily alkanes and partial oxidation of simple alkanes or mixtures containing primarily alkanes can be made to produce various blends that contain as principal products both alkenes and alkynes. Products in lower abundance will often include diolefins, compounds containing both yne and ene functionalities, polyenes, and other unsaturated moieties. Most commonly the desired products are the singly dehydrated compounds containing a single ene functionality. Thus, it is desirable to convert the alkynes to alkenes, but not convert the desired alkenes further to alkanes. Reactions of alkenes are generally more controllable than those of alkynes and diolefins, which tend to create oligomers and undesirable polyfunctional compounds.

The hydrogenation step is normally carried out on the primary gas produced in the cracking or pyrolysis reaction of natural gas and low molecular weight hydrocarbons, which includes all the initial gas products, also known as "front-end" hydrogenation, or subsequent to fractionation of the gas components, wherein the only stream subjected to hydrogenation is enriched in the highly unsaturated compounds, also known as "tail-end" hydrogenation. The advantage of primary gas hydrogenation is generally an abundance of the hydrogen required for hydrogenation. However, the excess available hydrogen in front-end hydrogenation can result in "run-away" reactivity wherein conversion of alkenes to alkanes reduces the value of the product. Fractionation reduces the available hydrogen but polymer formation is common, the effect of which is to shorten the useful life of the catalyst.

There are numerous examples of gas-phase hydrogenation of alkynes. For example, U.S. Patent No. 6,127,310 by Brown, et al. teaches that the selective hydrogenation of alkynes, which frequently are present in small amounts in alkene-containing streams (e.g., acetylene contained in

ethylene streams from thermal alkane crackers), is commercially carried out in the presence of supported palladium catalysts in the gas-phase.

In the case of the selective hydrogenation of acetylene to ethylene, preferably an alumina-supported palladium/silver catalyst in accordance with the disclosure in U.S. Patent No. 4,404,124 and its division U.S. patent 4,484,015 is used. The operating temperature for this hydrogenation process is selected such that essentially all acetylene is hydrogenated to ethylene (and thus removed from the feed stream) while only an insignificant amount of ethylene is hydrogenated to ethane. Proper temperature selection and control results in minimization of ethylene losses and allows one to avoid a runaway reaction, which is difficult to control.

U.S. Patent No. 5,856,262 describes use of a palladium catalyst supported on potassium doped silica wherein acetylene ranging in concentration from 0.01% to 5% in blends of ethylene and ethane is converted to ethylene in the gas-phase. U.S. Patent No. 6,350,717 describes use of a palladium-silver supported catalyst to hydrogenate acetylene to ethylene in the gas-phase. The acetylene is present at levels of 1% in a stream of ethylene. U.S. Patent No. 6,509,292 describes use of a palladium-gold catalyst wherein acetylene contained in a stream of principally ethylene, hydrogen, methane, ethane and minor amounts of carbon monoxide converts acetylene to ethylene in the gas-phase.

U.S. Patent No. 6,395,952 describes recovery of olefins from a cracked gas stream using metallic salts and ligands. The cracked gas stream is hydrogenated prior to scrubbing to remove acetylene from the stream.

U.S. Patent No. 5,587,348 describes hydrogenation of C_2 to C_{10} alkynes contained in comparable streams of like alkenes over a supported palladium catalyst containing fluoride and at least one alkali metal. Examples show hydrogenation of low concentrations of acetylene, below 1%, being converted to ethylene in a gas principally comprised of methane and ethylene at 200 psig and 130°F and 180°F. Care was taken to avoid heating the gas to a runaway temperature, wherein at least 4.5% of the ethylene would be converted to ethane and the temperature would become uncontrollable, which varied from about 70°F to 100°F above the minimum temperature that would reduce the acetylene concentration to acceptable levels.

U.S. Patent No. 6,578,378 describes a complex process for purification of ethylene produced from pyrolysis of hydrocarbons wherein the hydrogenation follows the tail-end hydrogenation technique. At the top of the de-ethanizer the vapor of the column distillate is treated directly in an acetylene hydrogenation reactor, the effluent containing virtually no acetylene being separated by a distillation column called a de-methanizer, into ethylene- and ethane-enriched tail product. The vapor containing acetylene is exposed to selective hydrogenation to reduce acetylene content of the

principally ethylene gas or treated with solvent to remove it and preserve it as a separate product. In all cases the acetylene content of the pyrolysis gas contained less than 1.5 mol% acetylene.

Hydrogenation is also known to occur in the liquid phase where the fluids are easily conveyed or transported as liquids under reasonable temperature and pressure. Naphtha cracking produces significant quantities of C₄ and C₅ unsaturated compounds, with 1,3 butadiene and 1-butene generally having the greatest commercial value.

U.S. Patent No. 6,015,933 describes a process in which polymer by-products from the steam cracking of naphtha to butadiene are removed. Acetylenes in the liquid hydrocarbon stream are selectively hydrogenated in a reactor to produce a reactor product containing at least hydrogen, butadiene, and polymer by-products having from about 8 to about 36 carbon atoms, and typically containing butenes and butanes. The acetylenic compounds are primarily vinyl acetylene, ethylacetylene, and methylacetylene. These acetylene group-containing molecules are converted to 1,3 butadiene, 1-butene, and propylene, but can react further with butadiene to form polymeric by-products. The reaction is carried out in the liquid phase with butadiene as the carrier. The undesirable feature of this process is that the carrier reacts with the products of the hydrogenation reaction, necessitating the removal of the polymeric by-products described.

U.S. Patent No. 5,227,553 describes a dual bed process for hydrogenating butadiene to butenes. This improvement is said to increase selectivity in streams containing high concentrations of butadiene while reducing the isomerization of butene-1 to butene-2, and nearly eliminating the hydrogenation of isobutene to isobutane as well as oligomerization.

U.S. Patent No. 4,547,600 discloses the need for more silver than previously thought necessary in the hydrogenation of acetylenic compounds that are found in butadiene as a result of steam cracking. The reaction is performed in the liquid phase where the product is the carrier.

U.S. Patent No. 3,541,178 reports a reduction in the loss of butadiene along with nearly complete reduction of acetylenic compounds by restricting the flow of hydrogen to no more than 80% to 90% of saturation in the hydrocarbon stream. This reduces the potential for polymerization of the vinylacetylenes, as there is no hydrogen remaining in the reaction stream at the end of the reaction. The undesirable aspect of this reduced hydrogen content however, is that the concentration of the hydrogen in the reactor is reduced, which decreases the reaction rate.

U.S. Patent No. 3,842,137 also teaches a reduction in the loss of butadiene to butene along with nearly complete conversion of vinylacetylene to butadiene, through the use of an inert diluent gas for the hydrogen. The hydrogen-containing gas includes no more than 25% hydrogen. The reaction takes place in the liquid phase, between a temperature of 40°F and 175°F, and at a pressure

of 80 to 200 psig. Again however, an undesirable aspect of using a diluent is that concentration of the hydrogen in the reactor is reduced, which decreases the reaction rate.

U.S. Patent No. 4,469,907 teaches high conversions of multiply unsaturated hydrocarbons to singly unsaturated hydrocarbons without subsequent isomerization, by staging the insertion of hydrogen into one or more reactors in series. An undesirable aspect of using several reactors however, is the increased complexity of the process, resulting in increased cost and more complicated process control.

There are several examples where non-linear and/or non-hydrocarbon compounds are hydrogenated in the liquid phase. For example, U.S. Patent No. 5,696,293 describes liquid phase hydrogenation and amination of polyols, carried out at pressures below 20 MPa using a supported ruthenium catalyst and containing another metal from Groups VIA, VIIA, and VIII. A ruthenium-palladium or singly palladium catalyst is listed in the examples. An undesirable feature of this process is the need to filter the fine and expensive catalyst out of the product. Catalyst losses are potentially very costly.

U.S. Patent No. 5,589,600 discloses hydrogenation of benzene to cyclohexene using ruthenium-nickel catalysts in the presence of water, which is purported to improve selectivity. U.S. Patent No. 5,504,268 discloses hydrogenation of aromatic acetylenic compounds that are impurities in vinyl aromatic compounds, over a supported palladium catalyst. The purported improvement is obtained via reduction of the hydrogen concentration by using a gas phase diluent such as nitrogen or methane. As previously noted, an undesirable aspect of using a diluent however, is the reduction in the concentration of hydrogen in the reactor and corresponding decrease in the reaction rate.

Carbon monoxide is known to enhance hydrogenation selectivity. It is added to a stream that has been thermally cracked or pyrolyzed to reduce the hydrogenation of the ene functional groups. U.S. Patent No. 6,365,790 describes an approach to selective hydrogenation of C_{10} to C_{30} alkynes to their respective alkenes in the liquid phase, by careful addition of a compound that decomposes to form CO. An undesirable aspect of using an additive is that the additive must later be removed from the product in diminished form.

U.S. Patent No. 4,517,395 indicates that CO and H_2 added to a liquid phase of C_{3+} multi-ene or mono-yne hydrocarbons, dispersed in the single-ene containing hydrocarbons, results in improved conversion due to better selectivity. The emphasis is on maintaining sufficient pressure to hold the CO and H_2 in the liquid phase rather than dispersed as a heterogeneous phase. Notably, water is added to reduce the amount of CO required as well as to reduce the temperature required.

U.S. Patent No. 4,705,906 presents a catalyst formulation wherein acetylene is converted by hydrogenation to ethylene, in the presence of CO in concentrations greater than 1 vol% in a

temperature range between 100°C and 500°C. The catalyst is a zinc oxide or sulphide, which may incorporate chromium, thorium, or gallium oxide. Zinc oxide and zinc sulphide were reportedly chosen for the reason that, although palladium catalysts are reasonably tolerant of the usual organic impurities which act solely as activity moderators, palladium catalysts are poisoned at low temperatures by high concentrations of carbon monoxide, such as those associated with unsaturated hydrocarbon-containing products obtained by the partial combustion of gaseous paraffinic hydrocarbons. This is to be contrasted with their behavior at low carbon monoxide concentrations, typically at concentrations less than 1 vol%, at which moderation of catalytic activity is reported to enhance the selectivity of acetylene hydrogenation to ethylene. At high temperature, palladium catalysts are active even in the presence of carbon monoxide, but selectivity of acetylene hydrogenation to ethylene is drastically reduced by simultaneous hydrogenation of ethylene to ethane.

In U.S. Patent No. 4,906,800, a Lindlar catalyst was used with a feed that contained no CO. The catalyst contained 5% palladium on a CaCO_3 support with about 3% lead as a promoter. After special treatment involving oxidation, reduction in CO, and finally a heat treatment step of the readily oxidized and reduced Lindlar catalyst, the treated catalyst showed improved selectivity at high conversion, but again at higher temperatures above 200°C selectivity decreased significantly.

U.S. Patent No. 5,847,250 describes a supported palladium catalyst employing a "promoter" from Groups 1 or 2 (in the New classification system; CAS Groups IA and IIA) and the palladium being supported on silica that has been pretreated to contain the promoter. The purported advantage is that no carbon monoxide is needed to provide increased selectivity because the selectivity-increasing effect of the carbon monoxide is strongly temperature dependent. Large temperature gradients in the catalyst bed therefore have an adverse effect on the selectivity when carbon monoxide is present. The reaction is performed in the gas phase in one or more beds with or without intermediate cooling or hydrogen gas addition. Acetylene content ranges from 0.01% to 5%. The reported selectivity ranges from 19 to 56%.

The use of liquid carriers has also been described in several patents for various reasons. For example, U.S. Patent No. 4,137,267 describes the hydrogenation of alkyl aminopropionitrile in the liquid phase, using hydrogen and ammonia as reactants over a supported catalyst and using an organic solvent. The solvent was selected to absorb excess heat by vaporizing at the process conditions, which is said to provide some temperature control. An undesirable aspect of employing a volatilizing solvent is the concomitant difficulty of employing this technique in a fixed catalyst bed.

U.S. Patent No. 5,414,170 teaches selective hydrogenation of a stream from an olefin plant after operation of a depropanizer but prior to operation of a de-ethanizer or de-methanizer. The hydrogenation is performed on the mixed-phase propane rich ethylene stream, as well as subsequently on the vapor product. A method is described by which the acetylenes in the front end of an olefin plant process stream are hydrogenated in the presence of a liquid hydrocarbon. The propane liquids, initially separated out of the inlet process stream, are used later to cool and wash the product of the acetylene hydrogenation reactor by adding them to the acetylene-containing stream during hydrogenation. An undesirable aspect of this process is the need to fractionate the propane from the small amount of ethylene produced.

U.S. Patent No. 5,059,732 discloses a process to hydrogenate effluent from a steam cracker containing ethylene, acetylene, propylene, propyne, propadiene, and butadiene, with hydrogen in the presence of a palladium or other noble metal catalyst by use of a gasoline cut as an inert carrier. The rationale for improved catalyst life is that the aromatic content of the gasoline carrier prevents plating out of the diolefins on the catalyst, which can otherwise polymerize and form gums that obstruct the other reactive components from getting to the catalyst surface. An undesirable aspect of this process however, is the need to fractionate the heavier hydrocarbon fraction from the small amount of ethylene produced, although this is not as serious a problem as when propane is used as the carrier.

Several patents disclose the use of solvents to separate the acetylenic fraction of a fluid stream from the other components. It is well known that dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) are good liquid absorbents for acetylene. Likewise, it is well known that DMF, furfural, ethylacetate, tetrahydrofuran (THF), ethanol, butanol, cyclohexanol, and acetonitrile are useful absorbents for 1,3-butadiene.

French Patent No. 2,525,210 describes a method for the purification of a stream containing mostly ethylene with a smaller amount of acetylene contaminant, wherein the acetylene is not converted to ethane. The basic concept is to hydrogenate a gas stream short of complete conversion, leaving some acetylene in the gas stream, then to absorb the acetylene in a solvent that extracts the acetylene from the ethylene stream. This extracted acetylene is separated from the solvent and recycled to the ethylene stream for hydrogenation. This is said to increase conversion to ethylene. An undesirable aspect of this process is the need to control the hydrogenation significantly below complete conversion.

U.S. Patent No. 4,277,313 focuses on the purification of a C₄ stream containing acetylenic compounds by hydrogenation of the acetylenic compounds followed by downstream separation. The hydrogenation step is carried out in the liquid phase after the hydrocarbon has been separated from

the absorbing solvent. It is said to be important to remove the acetylenic compounds prior to polymerization since they can form explosive metal acetylides and will cause the polymer to be off-spec. Suitable inert solvents for this process purportedly include: dimethylformamide (DMF), furfural, ethylacetate, tetrahydrofuran (THF), ethanol, butanol, cyclohexanol, and particularly acetonitrile.

U.S. Patent No. 3,342,891 describes fractionating a stream of C₄ and C₅ alkadienes into two streams, where one stream is reduced in vinyl acetylenes and the second stream is enriched in vinyl acetylenes. DMSO was used to separate the vinylacetylene from the enriched stream. The DMSO that contains the vinylacetylene was stripped with nitrogen to concentrate the vinylacetylene, which was subsequently hydrogenated in the gas phase. Unconverted vinyl acetylene in the effluent is recycled back to the feed of the fractionation column.

In some examples, the use of a liquid carrier or solvent is disclosed in which the liquid carrier or solvent is present during the hydrogenation step. U.S. Patent No. 4,128,595 for example, teaches a process wherein gaseous acetylene or acetylene group containing compounds are contacted with hydrogen via an inert saturated liquid hydrocarbon stream with hydrogenation occurring over a typical Group VIII metal supported on a catalyst medium. Examples of inert saturated hydrocarbons include various hexanes, decanes and decalin. The process requires the acetylene containing compound and saturated hydrocarbon solvent be fed co-currently into the top of a trickle bed reactor because the solubility of the acetylene containing compound in the saturated hydrocarbon solvent is poor at reaction conditions. An undesirable aspect of this process is the poor solubility of the hydrocarbon solvent toward acetylene. This patent teaches that rapid catalyst deactivation can occur with polar solvents. Dimethylformamide (DMF) was used as an absorbent for ethylene and the polar solvent during hydrogenation. The result indicated rapid catalyst deactivation with conversion dropping from 100% to 50% over a period of 17 hours. Accordingly, there is substantial need for a practicable liquid phase hydrogenation process, using satisfactory non-hydrocarbon solvents, if sufficient selectivity and conversion can be provided.

As is apparent, an efficient, practicable process for liquid-phase selective hydrogenation, with sufficient conversion and selectivity, would be a substantial contribution to the art. It has now been found that high alkyne conversion can be obtained with significant improvement in the selectivity to the corresponding alkene relative to the alkane in accordance with the present invention. Surprisingly, and contrary to the teachings of the conventional art relating to use of a polar solvent, such as dimethylformamide, a progressive decline in catalyst activity with time on stream is not observed with the inventive process, and excellent selectivity is obtained. In particular, the present invention exhibits increasing acetylene conversion to high steady state values, while

exhibiting excellent selectivity to ethylene, with sustained performance in operation for extended periods of time.

SUMMARY OF THE INVENTION

It is thus an object of this invention to overcome the deficiencies of the prior art and provide
5 a process for the selective hydrogenation of acetylene and acetylenic compounds wherein the
acetylene and/or acetylenic compounds are absorbed from a gas or liquid stream by use of a non-
hydrocarbon absorbent liquid to provide a reactant stream. The reactant stream comprising the
absorbent liquid containing the acetylene or acetylenic compounds is then exposed to a catalyst
10 comprising a Group VIII metal (using the CAS classification system) or combination of such
catalysts co-currently with a hydrogen-containing gas stream. It is consistent with this invention that
other gas or liquid components may be present in the reactant stream that contains acetylene or
acetylenic compounds, in major or minor proportions, and that these other components may include,
without limitation, aromatics, olefins, alkanes, water, alcohols, oxides, sulfides, and amines.
Typically, the non-hydrocarbon absorbents of this invention will be capable of absorbing in the range
15 of about 0.01 to about 100 (vol/vol) acetylene and/or acetylenic compounds. It is also consistent
with this invention that the non-hydrocarbon absorbents used to absorb acetylene or acetylenic
compounds from the aforementioned gas stream may comprise, without limitation: n-methyl-2-
pyrrolidone (NMP), acetone, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and
monomethylamine (MMA), and that the temperature and pressure selected for hydrogenation of the
20 acetylene or acetylenic compounds in the polar absorbent will be selected such that the liquid
absorbent does not form significant vapor.

It is also an object of this invention to obtain useful conversion of acetylene at relatively
moderate temperatures and pressures. Typically, the temperature may range from 0°F to 400°F and
the pressure may range from 1 to 2000 psia, wherein the choice of operating conditions will vary
25 depending on the absorbent chosen and the acetylenic compounds being hydrogenated, as will be
known to those skilled in the art. The temperature and pressure conditions employed in this
invention are typically sufficient to maintain the absorbent liquid in the liquid phase with at least a
portion of the acetylene and/or acetylenic compounds contained in the absorbent being
hydrogenated.

30 It is also an object of this invention that the acetylene and/or acetylenic compounds are
selectively hydrogenated to ethylene or homologous ethenic compounds with minimum conversion
to ethane and other saturated compounds.

It is also an object of this invention to provide operation of the reaction process in such a way
that "run-away" temperature conditions do not occur, and that temperature control is naturally

enhanced. The use of the aforementioned liquid absorbents acts to absorb more heat with less temperature rise, either at the catalyst surface or throughout the fluid phase, than a gas under most process conditions, due to a larger heat capacity per volume than the gas phase alone. These liquid absorbents also provide for improved heat transfer, as their thermal conductivity is much greater
5 under most process conditions.

It is also an object of this invention to obtain useful conversion of acetylene even in the presence of carbon monoxide well in excess of 1% of the non-absorbent components.

It is also an object of this invention to obtain useful conversion of acetylene in the presence of hydrogen equal to or in excess of that stoichiometrically required to effect the total hydrogenation
10 of the acetylene or acetylenic compounds.

It is also an object of this invention to perform absorption of acetylene from a mixed gas stream obtained from thermal or oxidatively enhanced cracking, prior to further separation of the gas components, in a commercially feasible manner.

It is also an object of this invention to perform the hydrogenation of acetylene and acetylenic
15 compounds in one or more reactors in series. Any catalyst known to selectively hydrogenate acetylene can be employed by this invention. The Group VIII metal hydrogenation catalysts are generally used and preferred. Most commonly, these are employed as supported catalysts on such materials as an alumina, a silica, or an aluminosilicate, but they may be supported as well on metal meshes or screens. Most commonly, these supports contain one or more Group VIII metals in the
20 amount of 0.01 to 10 percent by weight. There are many formulations of such catalysts which contain other components, primarily Group I through Group VII metals which improve selectivity, conversion, and/or yield. Accordingly, catalysts useful for the present invention may comprise Group VIII metal co-formulated with metals from Groups I through VII. Other applicable catalysts include but are not limited to nickel arsenide on alumina, ruthenium on alumina, Raney-nickel, zinc
25 oxide, and zinc sulphide.

It is also an object of this invention to perform the hydrogenation in a liquid or dispersed phase, such that separation can be effected by conventional means including, without limitation: distillation, single stage flash, multistage flash, crystallization, washing with a solvent, partitioning with a non-solvent, or a combination of these common separation means, not exclusive of less
30 common techniques that are known to those skilled in the art.

BRIEF DESCRIPTION OF THE DRAWING

The invention, together with further advantages thereof, may best be understood by reference to the following description taken in conjunction with the accompanying drawing in which:

The Figure is a simplified flow diagram of a selective hydrogenation process in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention thus provides, in a preferred embodiment, a process for the selective
5 hydrogenation of acetylene and/or acetylenic compounds wherein the acetylene and/or acetylenic
compounds are absorbed from a gas or liquid stream by use of a non-hydrocarbon absorbent liquid to
provide a reactant stream. Thereafter the reactant stream comprising the absorbent liquid, which
contains the acetylene or acetylenic compounds, is exposed to one or more Group VIII catalysts or
mixtures of known Group VIII catalysts that may be co-formulated with other metals, such as those
10 from Groups I through VII, or other known hydrogenation promoting catalysts. The reactant stream
may preferably be contacted with the catalyst(s) via any of the known reactor systems within the
discretion of one skilled in the art, including, without limitation, slurry bubble column reactors,
trickle bed reactors, three phase fluidized beds, fixed or moving bed reactors, riser reactors, fast-
fluidized beds, or any other reaction system, so long as the reactant stream and catalyst are contacted
15 under conditions suitable for hydrogenation and at a pressure and temperature sufficient to maintain
the absorbent liquid in the liquid phase, with at least a portion of the acetylene and/or acetylenic
compounds contained in the absorbent being hydrogenated, without departing from the scope of the
invention. The size, capacity, and scope of any particular embodiment of the inventive process to be
implemented may be determined following standard engineering practices well-known to those
20 skilled in the art and following performance data presented herein.

The absorption step may typically be performed at a temperature in the range of about 0°F to
about 400°F, a pressure in the range of about 1 psia to 2000 psia, wherein hydrogen is furnished in
sufficient quantity to hydrogenate at least a portion of the acetylene and/or acetylenic compounds.
The non-hydrocarbon absorbent liquid is typically capable of absorbing in the range of about 0.01 to
25 100 vol/vol acetylene and/or acetylenic compounds at standard conditions of temperature and
pressure (STP). Any of the conventional techniques to accomplish the absorption that are known to
those skilled in the art may be employed without departing from the scope of the invention.

Carbon monoxide may be contained in a stream comprising hydrogen or a hydrogen-
containing gas, or may be fed concurrently or simultaneously with the hydrogen required for
30 hydrogenation, and is typically present in concentration in the range of about 0.01 % to 300% of the
stoichiometrically required amount of hydrogen.

The non-hydrocarbon liquid absorbent may comprise, without limitation: n-methyl-2-
pyrrolidone (NMP), acetone, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), monomethylamine
(MMA), and/or combinations thereof, and is preferably NMP. The hydrogenation may preferably be

effected by passing the absorbed acetylene and/or acetylenic compounds into the inlet of a fixed bed reactor, or a series of reactors, containing the catalyst, while co-currently passing a stream of gas containing at least hydrogen into the reactor at an inlet location.

The source of acetylene and/or acetylenic compounds and/or hydrogen and/or carbon monoxide may preferably be pyrolysis, thermal cracking, steam cracking, partial oxidation, or other like process, wherein hydrocarbons or hydrocarbon-containing streams are thermally and/or chemically modified to produce increased quantities of unsaturated components, and the acetylene and/or acetylenic compounds may comprise, but are not limited to: acetylene, allene, vinyl acetylene, methyl acetylene, ethyl acetylene, 1-butyne, 2-butyne, and 1,3-butadiyne.

The Group VIII catalyst or mixture of Group VIII catalysts which may be co-formulated with other metals such as those from Groups I through VII is preferably a supported catalyst comprising about 0.01% to 10% Group VIII metal or about 0.01% to 10% Group VIII metal and 0.01% to 10% Group I through Group VII metal. The catalyst may comprise Raney nickel, palladium on alumina, ruthenium on alumina, nickel arsenide on alumina, zinc oxide, zinc sulphide, and mixtures of one or more of the above, in addition to other catalysts as are known to those skilled in the art. The catalyst may also comprise palladium/gold on alumina or the Lindlar catalyst. In another embodiment, the catalyst may preferably be palladium/gallium on alumina and/or palladium/indium on alumina and/or palladium/zinc on alumina.

In another preferred embodiment, the reactant stream may be exposed to a catalyst or catalysts as described in our co-filed application Ser.No. __/_____, entitled "Catalyst Formulation for Hydrogenation" by Marvin M. Johnson, Edward R. Peterson, and Sean C. Gattis, hereby incorporated by reference herein in its entirety.

In another preferred embodiment, the present invention comprises a process for recovering hydrogenated product from the liquid absorbent by distillation, wherein the hydrogenated stream is passed into a distillation column that is operated such that at least 90% of the hydrogenated product is recovered as a gas from the top of the distillation column, as will be known to those skilled in the art.

In another preferred embodiment, the present invention further includes a process for recovering hydrogenated product from the liquid absorbent by staged flashing, wherein the hydrogenated stream is passed into a flash drum that is operated at a pressure and temperature such that at least 90% of the hydrogenated product is recovered as a gas from the top vent of the flash drum. More than one flash drum may be used at more than one set of pressure and temperature conditions, such that at least 90% of the hydrogenated product is recovered as a gas from the top vents of the flash drums.

In another preferred embodiment, the present invention includes a process for recovering hydrogenated product from the liquid absorbent by intimate mixing of the hydrogenated stream with a partitioning fluid such that the desired hydrogenated product is evolved from the absorbent liquid by exclusion due to the properties of the mixture, such that at least 90% of the hydrogenated product is recovered as a separate stream from the separator.

In another preferred embodiment, the present invention includes a process for recovering hydrogenated product from the liquid absorbent by distillation wherein the hydrogenated stream is passed into a distillation column operated such that at least 90% of the hydrogenated product is recovered as a liquid from the bottom of the distillation column.

In another preferred embodiment, the present invention includes a process for recovering hydrogenated product from the liquid absorbent by staged flashing, wherein the hydrogenated stream is passed into a flash drum operated at a pressure and temperature such that at least 90% of the hydrogenated product is recovered as a liquid from the bottom of the flash drum.

Additional and further variations of the embodiments of the present invention will be known to those of skill in the art based on the disclosure of the inventive process, and the application of such known engineering practice within the field of hydrogenation and, more particularly, the field of the selective hydrogenation of alkynes to their corresponding alkenes, to the aspects of the present invention should be considered to be within the scope of the present invention.

Referring now to the Figure, an acetylene solution of n-methyl-2-pyrrolidone (NMP) was first prepared by slowly bubbling pure acetylene from acetylene vessel 10 at atmospheric pressure via valve 110 into a weighed and tared NMP vessel 20 containing NMP. The NMP containing acetylene was then drawn through valve 120 by pump 410 and pumped to reactor 200 comprising tubular reaction vessel 230 comprising a one-half inch (OD) stainless steel tube containing a supported catalyst 210. Co-currently, a gas containing hydrogen from vessel 30 and carbon monoxide from vessel 40 was flowed under pressure at a controlled rate using flow controllers 330 and 340, and corresponding control valves 130 and 140, and was mixed with the NMP stream containing acetylene from the outlet of pump 410. The fluid mixture comprising NMP, acetylene, hydrogen, and CO was allowed to flow at a controlled rate and under pressure control into reaction vessel 230 of reactor 200, containing the fixed bed of supported catalyst 210. The reactor temperature was controlled by an external heating element (not shown) surrounded by insulation 220. The fluid temperature was measured prior to its entering the reactor and upon leaving the reactor by temperature sensors (not shown). The reaction temperature was measured near the center of the fixed bed of catalyst 210 via a 1/8 inch thermowell and temperature indicator 170. Reactor pressure, indicated by pressure indicator 160 was controlled by a pressure control device (calibrated

and self-regulating mechanical spring-type) 150. The reactor fluid cooled upon exiting the reactor, and a gas-liquid separation was made in knock-out pot 630 at 80°C. The overhead gas from knock-out pot 630 flowed through pressure control device 150, and was cooled to -79°C in dry ice trap 510 to collect all remaining components except those that remain a gas at this temperature and pressure, such as hydrogen, nitrogen, argon, and methane, and was then sent to gas chromatograph 610 to provide quantitative analysis of the gas composition. The liquid stream, comprising NMP, C₂, C₄, and heavier components was collected in knock-out pot 630, and was periodically sampled via ice bath 620, and was also analyzed by gas chromatograph 610 to obtain quantitative composition analysis.

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

EXAMPLES

Selective Hydrogenation Catalyst Preparation

A number of experimental catalysts were prepared by incipient wetness impregnation of a commercially available "skin" catalyst (also known in the art as "rim" or "eggshell" catalysts) that contained from 0.3 to 0.7 wt-% palladium concentrated near the exterior surface of roughly spherical particles of alumina, which had been heat treated to reduce microporosity. For example, a commercially available catalyst originally available from Mallinckrodt Chemicals, product number E144SDU, containing about 0.5 wt-% Pd on roughly spherical 1/16" diameter alumina particles, with a surface area of about 40-70 m²/gm and a pore volume of about 0.5 may be used. Similar catalysts commercially available from Engelhard and Calsicat (such as 1435DU) may also be used. Several of the experimental catalysts described below were crushed and then double-screened between 40 and 50 mesh (USS or U.S. sieve series) screens, thus providing catalyst particles with a minimum dimension in the range of from about 0.0117 to about 0.0165 inches. Those skilled in the art will recognize that other known catalysts and supports may likewise be employed without departing from the scope of the invention. Most of the experimental catalysts described below involved dissolving the nitrate salt of the promoter in the amount of water required to just fill the internal pores of the catalyst support, though other techniques as are known in the art may of course be employed.

Example 1

Catalyst containing 0.3 wt-% Pd/Al₂O₃. A commercially available Engelhard catalyst that contained 0.3 wt-% Pd/Al₂O₃ was used for this Example. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. The catalyst was dried for one

hour. The dried product was reduced in place at 100 °C and 250 psig for two hours with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 2

5 Catalyst containing 0.3 wt-% Pd/Al₂O₃. Preparation of this catalyst began with the Engelhard catalyst of Example 1 that contained 0.3 wt-% Pd/ Al₂O₃. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. The catalyst was dried for one hour, crushed and double-screened between 40 and 50 mesh (USS) screens, and reduced in place at 400 °C and 150 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 3

10 Catalyst containing 0.7 wt-% Pd/Al₂O₃. Preparation of this catalyst began with an Engelhard catalyst which contained 0.7 wt-% Pd/ Al₂O₃. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. The catalyst was reduced in place at 50 °C and 250 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 4

15 Catalyst containing 0.3 wt-% Pd – 1.2 wt-% Au/Al₂O₃. Preparation of this catalyst began with the Engelhard catalyst of Example 1 that contained 0.3 wt-% Pd/Al₂O₃. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst particles were dropwise impregnated with a gold chloride solution, dried at 150°C for one hour, and calcined at 300°C for one hour to produce a 1.2 wt-% Au - 0.3 wt-% Pd/Al₂O₃ product. The product was crushed and double-screened between 40 and 50 mesh (USS) screens, and reduced in place for one hour at 100 °C and 250 psig with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 5

25 Catalyst containing 0.3 wt-% Pd – 0.3 wt-% Ag/ Al₂O₃. Preparation of this catalyst began with a Calsicat catalyst that contained 0.3 wt-% Pd/ Al₂O₃. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. For this Example, 10 grams of the Calsicat catalyst was dropwise impregnated with 0.047 grams of AgNO₃ dissolved in 5 ml of water, dried for one hour at 150 °C, and calcined at 300°C for one hour to give a 0.3% Ag - 0.3% Pd/ Al₂O₃ product. The product was then crushed and double screened between 40 and 50 mesh (USS) screens and reduced in place at 100°C and 250 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 6

30 Catalyst containing 0.3 wt-% Pd – 0.6 wt-% Ag/Al₂O₃. Preparation of this catalyst began with the Calsicat catalyst of Example 5 that contained 0.3 wt-% Pd/Al₂O₃. The alumina supported

catalyst particles were roughly spherical and approximately 1/16 inches in diameter. For this Example, the procedure of Example 5 was followed except that the concentration of silver nitrate in the impregnating solution was twice that of Example 5. The product was again dried for one hour at 150°C, and calcined at 300°C for one hour. The 0.6% Ag - 0.3% Pd/ Al₂O₃ product was then
5 crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at 100°C and 250 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 7

Catalyst containing 0.3 wt-% Pd – 0.1 wt-% Mn/Al₂O₃. This catalyst was prepared from an Engelhard catalyst that contained 0.3 wt-% Pd/Al₂O₃. The alumina supported catalyst particles were
10 roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst was dropwise impregnated with manganese acetate, dried at 150°C and calcined at 300°C to give a 0.3 wt-% Pd - 0.1 wt-% Mn/Al₂O₃ product. The calcined product was then crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at 300°C and 250 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 8

Catalyst containing 0.3 wt-% Pd – 0.385 wt-% In/Al₂O₃. This catalyst was prepared from the Engelhard catalyst that contained 0.3 wt-% Pd/Al₂O₃. The alumina supported catalyst particles were
15 roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst was dropwise impregnated with an aqueous solution of indium nitrate, dried at 150°C for one hour, and
20 calcined at 300 °C for one hour to give a 0.3 wt-% Pd - 0.4 wt-% In/Al₂O₃ product. The calcined product was then crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at 300-314°C and 250 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 9

Catalyst containing 0.3 wt-% Pd – 0.26 wt-% Ga/Al₂O₃. This catalyst was prepared from the Engelhard catalyst that contained 0.3 wt-% Pd/Al₂O₃. The alumina supported catalyst particles were
25 roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst was dropwise impregnated with an aqueous solution of gallium nitrate, dried at 150°C for one hour, and
calcined at 300°C for one hour to give 0.3 wt-% Pd - 0.26 wt-% Ga/Al₂O₃ product. The product was then crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at
30 400°C and 250 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Example 10

Catalyst containing 0.5 wt-% Pd – 0.5 wt-% Zn/Al₂O₃. Preparation of this catalyst began with a palladium catalyst from Calsicat (product number E144SDU) containing 0.5 wt-% Pd/Al₂O₃. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in

diameter. The palladium-containing material was then dropwise impregnated with a solution of zinc formate, dried for one hour at 150°C, and calcined at 300°C for one hour to give a 0.5 wt-% Pd - 0.5 wt-% Zn/Al₂O₃ product. The product was then crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at 400-420°C and 250 psig for one hour with a 2:1 H₂:CO gas mixture (66% H₂ - 34% CO).

Selective Hydrogenation of Acetylene - Experimental Catalysts

Example 11

A reactor in accordance with an embodiment of the invention described above and in the drawing Figure was constructed for the tests described below. Approximately 3 cm³ of catalyst was diluted with 6 cm³ of inert low surface area alumina (alundum) as a catalyst surface area diluent, and placed into the reaction vessel in a fixed bed configuration. Other catalyst surface area diluents may of course be used, as will be known to those skilled in the art. The catalyst was placed in the center section of the reaction vessel between two six-inch deep beds of 3 mm glass beads, one placed upstream of the catalyst for preheat purposes and one downstream, in the exit section.

The operating conditions are as shown in Table 1. The liquid reactant flow rate was set at 18 ml/hr of NMP containing 4.2 wt-% dissolved acetylene. A 2:1 H₂:CO gas mixture was used and the H₂/C₂H₂ ratio was 1.56:1. Product gas analyses (for C₂ components only) were obtained after removal of the NMP and after the composition of the product gas had reached steady state and subsequent samples showed no significant change in composition. The gas composition results are shown in Table 1. The product gas concentrations do not sum to 100% due to the presence of other components in minor amounts and measurement error. The mass balance closure for these results is estimated at about 95%.

For comparison purposes, the selectivity of ethylene to ethane may be estimated by the ratio of the product ethylene concentration to the concentration of ethane, defined here as the screening selectivity S_s (and presented in Table 1) as $S_s = [C_2H_4] / [C_2H_6]$. Also for comparison purposes, the relative acetylene conversions may be estimated from the product acetylene concentrations. This is defined here (and also presented in Table 1) as the screening conversion $S_c = 100 - [C_2H_2]$ where the acetylene concentration is expressed in per cent.

The data shown in Table 1 thus describe representative results for catalytic selective hydrogenation in accordance with the invention. As may be seen from examination of the data tabulated in Table 1, significant improvements in the selectivity to ethylene result from the addition of promoters at high acetylene conversion. Contrary to the teachings of the prior art, a progressive decline in activity with time on stream was not observed. The gallium and indium containing catalysts showed relatively high selectivity. Likewise, excellent selectivity and activity were

observed for catalysts prepared applying a promoter metal after first applying the Group VIII metal to the support. Accordingly, the catalytic process of the present invention provides improved conversion and selectivity in selective hydrogenation of acetylene dissolved in NMP. The indium-promoted catalyst and, to a lesser extent, the gallium-promoted catalyst is effective with palladium on alumina, and both exhibit higher selectivity to ethylene than either the traditional silver-promoted or gold-promoted catalysts used to advantage for the removal of acetylene in ethylene by selective hydrogenation in the front-end gas phase hydrogenation process.

Table 1

Catalyst	Composition	T (°C)	P (psig)	H ₂ /CO Flow (ml/min)	Ethane (%)	Ethylene (%)	Acetylene (%)	S _s	S _c (%)
Example 1	0.3% Pd on 1/16" alumina spheres	111	250	30	10.0	89.4	0.5	8.9	99.5
Example 2	0.3% Pd on 40-50 mesh alumina particles	128	150	35	2.6	94.0	0.80	36	99.2
Example 3	0.7% Pd on 1/16" alumina spheres	111	250	40	6.4	93.4	0.1	15	99.9
Example 4	0.3% Pd – 1.2% Au on 40-50 mesh alumina particles	120	250	35	6.25	93.50	0.15	15	99.9
Example 2	0.3% Pd on 40-50 mesh alumina particles	119	250	32	2.42	91.0	6.34	38	93.7
Example 5	0.3% Pd – 0.3% Ag on 40-50 mesh alumina particles	114	250	30	3.68	93.5	2.77	25	97.2
Example 6	0.3% Pd – 0.6% Ag on 40-50 mesh alumina particles	115	250	30	3.33	96.2	0.41	29	99.6
Example 7	0.3% Pd – 0.1% Mn on 40-50 mesh alumina particles	122	250	30	3.91	95.6	0.42	24	99.6
Example 8	0.3% Pd – 0.385% In on 40-50 mesh alumina particles	137	250	30	1.46	96.8	1.70	66	98.3
Example 9	0.3% Pd – 0.26% Ga on 40-50 mesh alumina particles	130	250	30	2.02	97.5	0.40	48	99.6

Selective Hydrogenation of Acetylene—Sustained Activity of Indium-Promoted Palladium Catalyst

Example 12

The results obtained from Example 11 and shown in Table 1 were considered promising. Therefore, an extended duration run was made with an indium-containing catalyst similar to that of Example 8 but with 0.22 wt-% indium to determine whether this high selectivity catalyst would also have sustained activity for selective hydrogenation. Operating conditions for the sustained activity tests included: reactor pressure of 150 psig; 1.5 wt-% acetylene was absorbed and dissolved in the NMP absorbent to provide the reactant stream; the molar ratio of H₂ to C₂H₂ was set at 1.26:1; and the flowrate of reactant through the bed (liquid hourly space velocity) was set to an LHSV of 5 hr⁻¹.

The catalyst was operated for about 143 hours, and product gas composition was determined at selected intervals, as shown in Table 2. It is estimated that the mass balance closure for these results was about 95 %.

Table 2

Time on Stream (hrs)	70	104
Temperature (°C)	134	134
Pressure (psig)	150	150
Methane (wt-%)	0.01	0.01
Ethane (wt-%)	1.30	1.19
Ethylene (wt-%)	97.50	98.10
Acetylene (wt-%)	0.39	0.08
Trans-2-butene (wt-%)	0.07	0.06
1-butene (wt-%)	0.21	0.17
Cis-2-butene (wt-%)	0.07	0.06
Butadiene (wt-%)	0.40	0.31
Total (wt-%)	99.95	99.98
S_s	75	82
S_c (%)	99.6	99.9

After this extended run, the catalyst bed was flushed with nitrogen at 425°C and the catalyst was oxidized in air for one hour. The catalyst was then reduced with the 2:1 H₂:CO mixture at 417°C and 150 psig, and tested again to determine whether it was active. The catalyst was again both active and selective for the selective hydrogenation of acetylene dissolved in NMP with a H₂ and CO mixture.

Selective Hydrogenation of Acetylene – Zinc-Promoted Palladium Catalyst**Example 13**

This example was performed under conditions similar to those of Example 11, using the catalyst prepared as described in Example 10. The reactant stream comprised 1.5 wt-% acetylene in NMP. The H₂:CO feed ratio was 2:1 (vol/vol). The H₂:C₂H₂ to the reactor was 2.76:1. The reaction pressure was maintained at approximately 250 psig and the average temperature in the catalyst bed was 128°C. The reactant stream flow rate was set to a LHSV of 5 hr⁻¹.

Table 3 provides results from these tests in the form of product gas composition as a function of reaction time. It is estimated that the mass balance closure for these results was about 98-99 %. As will be seen from the results in Table 3, the process of the present invention provides improved ethylene selectivity at high acetylene conversion with the zinc-promoted catalyst.

Table 3

Time (hr)	CH ₄ (wt-%)	C ₂ H ₆ (wt-%)	C ₂ H ₄ (wt-%)	C ₂ H ₂ (wt-%)	t-C ₄ H ₈ (wt-%)	i-C ₄ H ₈ (wt-%)	c-C ₄ H ₈ (wt-%)	1,3- C ₄ H ₈ (wt-%)	S _s	S _c (%)
0.5	0.04	0.91	97.4	0.48	0.04	0.09	0.07	0.85	107	99.5
1.0	0.02	0.87	97.4	0.37	0.05	0.09	0.08	1.00	112	99.6
1.5	0.02	0.85	97.5	0.29	0.05	0.09	0.07	1.00	115	99.7
2.0	0.01	0.84	97.6	0.24	0.04	0.09	0.07	1.00	115	99.8
2.5	0.01	0.83	97.7	0.21	0.04	0.08	0.06	0.97	118	99.8
3.0	0.01	0.82	97.8	0.20	0.04	0.08	0.06	0.93	119	99.8
3.5	0.01	0.81	97.9	0.18	0.04	0.07	0.06	0.89	121	99.8
4.0	0.01	0.81	98.0	0.16	0.03	0.07	0.05	0.83	121	99.8
4.5	0.01	0.80	98.1	0.14	0.03	0.07	0.05	0.77	123	99.9
5.0	0.01	0.79	98.2	0.12	0.03	0.06	0.04	0.72	124	99.9

Selective Hydrogenation of Acetylene – Sustained Activity of Zinc-Promoted Palladium Catalyst**Example 14**

This example was again performed using the catalyst of Example 10. The test was performed under conditions similar to those of Example 13 but with the following differences. The reactant stream flow rate was set to a LHSV of 10 hr⁻¹. The average catalyst bed temperature was 140°C, and the H₂:C₂H₂ to the reactor was 3.7:1.

The results of this test are provided in Table 4 in the form of gas composition. The gas composition data are the result of gas analyses only; when the C₄ compounds that collect in the liquid are combined with those in the gas phase, 3.14 wt-% of the acetylene reacted goes to form C₄ compounds initially, but this figure drops to 2.31 wt-% after 14 hours of operation and levels off to

about 2.1 wt-% after about 21 hours of operation. It is estimated that the mass balance closure for these results was about 98%-99%.

Accordingly, the progressive decline in activity with time on stream predicted by the conventional art is not observed with the process of the present invention. Indeed, the results of Table 3 indicate improvement in conversion and selectivity with time on stream for the inventive process using the catalyst of Example 10.

Table 4

Time (hr)	CH ₄ (wt-%)	C ₂ H ₆ (wt-%)	C ₂ H ₄ (wt-%)	C ₂ H ₂ (wt-%)	C ₄ H ₈ (wt-%)	1,3- C ₄ H ₈ (wt-%)	S _s	S _c (%)
7	0.06	0.33	97.4	1.20	0.07	0.87	295	98.8
14	0.07	0.60	98.1	0.68	0.10	0.43	164	99.3
21	0.02	0.60	98.2	0.77	0.02	0.31	164	99.2
24	0.02	0.50	98.6	0.33	0.02	0.38	197	99.7

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modification thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process design criteria, pendant processing equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Description of the Related Art is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

WE CLAIM:

1. A selective hydrogenation process, comprising:
preparing a reactant stream comprising an alkyne absorbed in a liquid absorbent;
contacting the reactant stream with a selective hydrogenation catalyst in the presence of a gas
5 stream comprising hydrogen at hydrogenation conditions to provide a product stream;
separating the absorbent from the product stream to recover a product.
2. The process of claim 1 wherein the liquid absorbent is selected from the group consisting of
NMP, acetone, THF, DMSO, MMA, and combinations thereof.
3. The process of claim 2 wherein the catalyst comprises a supported Group VIII metal.
- 10 4. The process of claim 3 wherein the catalyst further comprises a second metal selected from
the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals,
and combinations thereof.
5. The process of claim 4 wherein the gas stream further comprises carbon monoxide.
6. The process of claim 5 wherein the second metal comprises a metal selected from the group
15 consisting of Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof.
7. The process of claim 6 wherein the second metal comprises a metal selected from the group
consisting of In, Ga, Mn, and Zn.
8. The process of claim 7 wherein the liquid absorbent comprises NMP.
9. The process of claim 8 wherein the second metal comprises Zn.
- 20 10. A selective hydrogenation process, comprising:
contacting an alkyne absorbed in a liquid absorbent with a catalyst in the presence of a
hydrogen-containing stream at conditions conducive to selective hydrogenation to produce a product
stream comprising a product alkene;
separating the liquid absorbent from the product stream to substantially recover the product
25 alkene.
11. The process of claim 10 wherein the liquid absorbent is selected from the group consisting of
NMP, acetone, THF, DMSO, MMA, and combinations thereof.
12. The process of claim 11 wherein the selective hydrogenation catalyst comprises a supported
Group VIII metal.
- 30 13. The process of claim 12 wherein the selective hydrogenation catalyst further comprises a
second metal selected from the group consisting of Group IIB metals, Group IIIA metals, Group
VIIB metals, and combinations thereof.
14. The process of claim 13 wherein the second metal comprises a metal selected from the group
consisting of In, Ga, Mn, and Zn.

15. The process of claim 14 wherein the liquid absorbent comprises NMP.

16. The process of claim 15 wherein the second metal comprises Zn.

17. A process for the selective hydrogenation of alkynes comprising:

absorbing one or more alkynes in a liquid absorbent to provide a reactant stream;

5 contacting said reactant stream with a catalyst in the presence of a hydrogen-containing gas stream at hydrogenation conditions to produce a product stream comprising the alkene analogs of the one or more alkynes;

separating said alkene analogs from said product stream.

18. The process of claim 17 wherein the liquid absorbent is selected from the group consisting of
10 NMP, acetone, THF, DMSO, MMA, and combinations thereof.

19. The process of claim 18 wherein the liquid absorbent is NMP.

20. The process of claim 19 wherein the hydrogen-containing gas stream further comprises carbon monoxide.

21. The process of claim 19 wherein the catalyst comprises a Group VIII metal and a catalyst
15 support.

22. The process of claim 21 wherein the catalyst further comprises a second metal selected from the group consisting of Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof.

23. The process of claim 22 wherein the second metal is selected from the group consisting of In,
20 Ga, Mn, and Zn.

24. The process of claim 23 wherein the catalyst support comprises a particulate alumina.

25. The process of claim 24 wherein the catalyst comprises Zn.

26. A process for the selective hydrogenation of acetylenic compounds, comprising:

25 absorbing one or more acetylenic compounds in a liquid polar non-hydrocarbon absorbent to provide a reactant stream;

contacting the reactant stream with a hydrogenation catalyst in the presence of a gas stream comprising hydrogen under selective hydrogenation conditions to provide a product stream, wherein said product stream comprises the ethylenic compounds corresponding to the one or more acetylenic compounds in the reactant stream;

30 separating the absorbent from the product stream.

27. The process of claim 26 wherein the liquid polar non-hydrocarbon absorbent comprises NMP.

28. The process of claim 27 wherein the gas stream further comprises carbon monoxide.

29. The process of claim 27 wherein the hydrogenation catalyst comprises a zinc-promoted palladium catalyst on an alumina support.

30. The process of claim 27 wherein the hydrogenation catalyst comprises a promoter selected from the group consisting of In, Ga, Mn, Zn, and combinations thereof.

31. The process of claim 30 wherein the selective hydrogenation conditions comprise a temperature of from 100°C to 150°C, a pressure of from 100 psig to 400 psig, a H₂:CO of from 1:1 to 3:1, and a H₂:C₂H₂ of from 1:1 to 5:1.

32. The process of claim 31 wherein the promoter comprises Mn or Zn.

33. The process of claim 32 wherein the promoter comprises Zn.

34. A process for the selective hydrogenation of alkynes, comprising:
preparing a liquid reactant stream comprising between 0.5 wt-% and 10 wt-% C₂H₂ dissolved in n-methyl-2-pyrrolidone;

contacting the reactant stream and a gas stream comprising a mixture of H₂ and CO in continuous flow with a catalyst at a feed ratio of H₂:C₂H₂ of from about 1:1 to about 5:1 at selective hydrogenation reaction conditions to produce a product stream,

separating substantially all of the n-methyl-2-pyrrolidone from the product stream;
recovering a product comprising C₂H₄.

35. The process of claim 34 wherein the catalyst comprises a supported Group VIII metal and a promoter selected from the group consisting of Group IIB metals, Group IIIA metals, and Group VIIB metals, and combinations thereof.

36. The process of claim 35 wherein the promoter is selected from the group consisting of In, Ga, Mn, Zn, and combinations thereof.

37. The process of claim 36 wherein the promoter is selected from the group consisting of In and Ga.

38. The process of claim 36 wherein the promoter is Mn.

39. The process of claim 36 wherein the promoter is Zn.

40. A process for the selective hydrogenation of alkynes, comprising:
absorbing an alkyne compound in a liquid polar non-hydrocarbon absorbent to provide a reactant stream;

contacting the reactant stream with a selective hydrogenation catalyst in the presence of a gas stream comprising hydrogen;

hydrogenating at least a portion of the alkyne compound to provide a product stream comprising an alkene compound corresponding to the alkyne compound;

substantially separating the absorbent from the product stream;
recovering a product comprising the alkene compound.

41. The process of claim 40 wherein 90% or more of the alkyne compound is hydrogenated to the corresponding alkene compound.

42. process of claim 41, further comprising passing the product stream to one or more distillation columns, wherein said one or more distillation columns are operated such that 90% or more of the alkene compound is recovered as a gas from the top of the one or more distillation columns.

43. The process of claim 41, further comprising passing the product stream to one or more flash drums, wherein said one or more flash drums are operated such that 90% or more of the alkene compound is recovered as a gas from the top vents of the one or more flash drums.

44. The process of claim 41, further comprising passing the product stream to one or more distillation columns, wherein said one or more distillation columns are operated such that 90% or more of the alkene compound is recovered as a liquid from the bottom of the one or more distillation columns.

45. The process of claim 41, further comprising passing the product stream to one or more flash drums, wherein said one or more flash drums are operated such that 90% or more of the alkene compound is recovered as a liquid from the bottom of the one or more flash drums.

46. The process of claim 41, further comprising mixing the product stream with a partitioning fluid wherein at least 90% of the alkene compound is evolved from the absorbent by exclusion.

47. The process of claim 41 wherein the liquid polar non-hydrocarbon absorbent is selected from the group consisting of NMP, DMF, acetone, THF, DMSO, MMA, and combinations thereof.

48. The process of claim 47 wherein the reactant stream is contacted with the selective hydrogenation catalyst in a reactor selected from the group consisting of slurry bubble column reactors, trickle bed reactors, three phase fluidized bed reactors, fixed bed reactors, riser reactors, fast-fluidized bed reactors, and combinations thereof.

49. The process of claim 47 wherein the reactant stream is contacted with the selective hydrogenation catalyst in a fixed bed reactor wherein the gas stream flows co-current to the reactant stream.

50. The process of claim 49 wherein the gas stream further comprises carbon monoxide.

51. The process of claim 50 wherein the reactor is operated at a temperature and pressure sufficient to maintain the absorbent in a liquid phase.

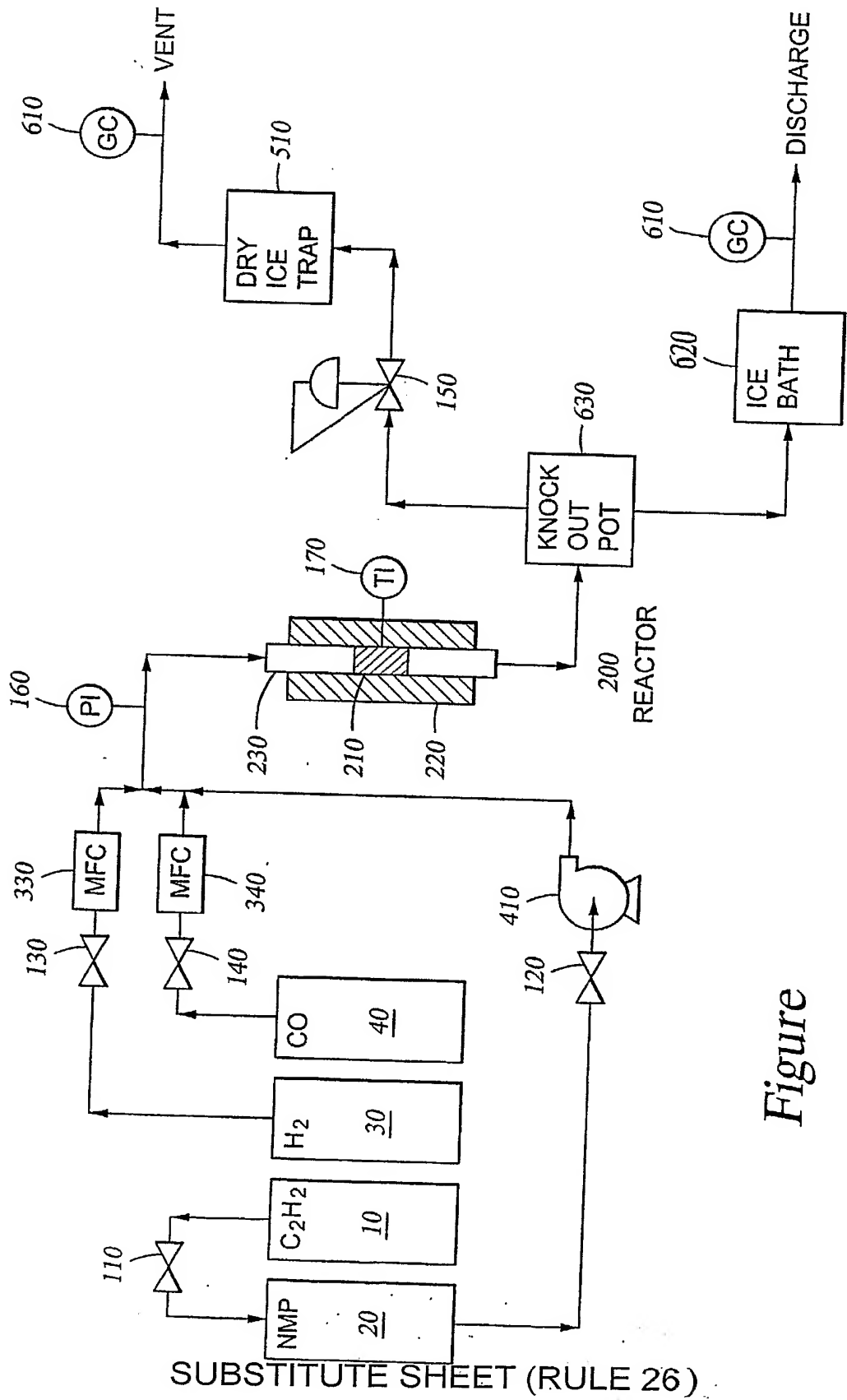
52. The process of claim 51 wherein the catalyst comprises a promoter selected from the group consisting of Group IIB metals, Group IIIA metals, and Group VIIB metals, and combinations thereof.

53. The process of claim 52 wherein the promoter is selected from the group consisting of In,
5 Ga, Mn, Zn, and combinations thereof.

54. The process of claim 53 wherein the promoter is Zn.

55. The process of claim 53 wherein the promoter is Mn.

56. The process of claim 53 wherein the promoter is selected from the group consisting of In, Ga, and combinations thereof.



Figure

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/38871

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C07C 5/02, 5/09, 7/10

US CL : 585/258, 259, 833, 864

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
U.S. : 585/258, 259, 833, 864

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,755,488 A (JOHNSON et al) 28 August 1973 (28.08.1973), see column 1, lines 12-25 and 65-68; column 2, lines 1-68; and column 3, lines 14-55.	1-3, 10-12, 17-19, 21, 26, 27, 40-49
Y		4-9, 13-16, 20, 22-25, 28-39, 50-56
Y	US 2002/0068843 A1 (DAI et al) 06 June 2002 (06.06.2002), see paragraphs 0013-0018.	4-9, 13-16, 22-25, 30-33, 36, 38, 39, 52-55
Y	US 5,356,851 A (SARRAZIN et al) 18 October 1994 (18.10.1994), see column 2, lines 3-36.	7, 8, 14, 15, 23, 30, 31, 36, 37, 53, 56
Y	US 6,365,790 B2 (REIMER et al) 02 April 2002 (02.04.2002), see column 3, lines 18-40.	5-9, 20, 28, 34-39, 50-56
A	US 6,358,399 B1 (MINKKINEN et al) 19 March 2002 (19.03.2002).	1-56

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

12 November 2004 (12.11.2004)

Date of mailing of the international search report

06 DEC 2004

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

PCT/US03/38871

Continuation of B. FIELDS SEARCHED Item 3:

EAST search terms: selective hydrogenation, acetylene, alkyne, solvent, absorbent, pyrrolidone, tetrahydrofuran, dimethylsulfoxide, monomethylamine